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(54) **NICKEL-IRON ALLOY PLATING SOLUTION**

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(57) **ABSTRACT**

A nickel-iron alloy plating solution which can suppress, in a nickel-iron alloy plating solution containing divalent iron ions and divalent nickel ions, oxidation of divalent iron ions to trivalent iron ions and can prevent the occurrence of the precipitation of iron (III) hydroxide to allow stable continuous operation and also to provide a nickel-iron alloy plating solution which allows production of a soft magnetic film which is stable in composition. The nickel-iron alloy plating solution of the present invention is characterized in that it comprises divalent iron ions, divalent nickel ions and a hydroxylamine salt and has a pH of 3.0 or lower.

2 Claims, No Drawings

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NICKEL-IRON ALLOY PLATING SOLUTION

TECHNICAL FIELD

The present invention relates to a nickel-iron alloy plating solution. 5

BACKGROUND ART

Magnetic thin films (soft magnetic thin films) having a low characteristic value of coercivity are widely used for electronic components such as magnetic heads, small transformers, meter gauges and magnetic shieldings. 10 15

Soft magnetic thin films such as cobalt based alloy films or permalloy films having an iron content of 50 to 60% by mass have high saturation magnetic flux density and are used for magnetic heads of AV. On the other hand, permalloy films having an iron content of around 20% by mass have low magnetic flux density; but due to their high initial magnetic permeability, they are used for small transformers, meter gauges, magnetic shieldings and the like. 20

Nickel-iron alloy films may be prepared by a method in which electroplating is carried out with a plating solution containing divalent iron ions and divalent nickel ions. 25

However, when a nickel-iron alloy plating solution containing divalent iron ions is left over, iron ions are oxidized to be trivalent iron ions and iron (III) hydroxide is precipitated. During plating, divalent iron ions are oxidized to trivalent iron ions at the anode side, resulting in the occurrence of the precipitation of iron (III) hydroxide. The precipitation of iron (III) hydroxide is dispersed in the plating solution and incorporated into a plating film, causing poor appearances or a decrease in the saturation magnetic flux density of the film. Accordingly, it is desirable to prevent the occurrence of the precipitation of iron (III) hydroxide. 30 35

The precipitation of iron (III) hydroxide during nickel-iron alloy electroplating may be suppressed, for example, by a method in which a compound capable of forming stable complex ions with trivalent iron ions such as a dicarboxylic acid is added to the plating solution (Patent document 1). By adding a dicarboxylic acid such as malonic acid and adjusting the pH to 1.5, trivalent iron ions are stabilized as complex ions and occurrence of the precipitation is suppressed. Although the added complexing agent such as malonic acid in this method can suppress occurrence of the precipitation, it cannot suppress the oxidation of iron ions from divalent to trivalent. As a result, a plating film having a stable composition cannot be obtained because the quantities of electricity required for deposition of the divalent and trivalent ions are different, and it is difficult to maintain the composition of iron at 18 to 22% by mass in the deposited film during plating. 40 45

It has been also known that an addition of a reducing agent can suppress the production of trivalent iron ions and allows stable continuous operation. For example, in Patent document 2, a reducing agent such as L-ascorbic acid and gallic acid is added to an iron group alloy plating solution and the pH is adjusted to 1 to 5, in order to suppress the production of trivalent iron ions. However, the occurrence of the precipitation of iron (III) hydroxide could not be sufficiently suppressed, even with the addition of a reducing agent such as L-ascorbic acid and gallic acid. 50 55 60

Accordingly, none of the above processes can sufficiently suppress the precipitation of iron (III) hydroxide in nickel- 65

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iron alloy electroplating solutions and there have been a difficulty in obtaining soft magnetic films.

PRIOR ART

Documents Patent Documents

Patent document 1: Japanese Patent Publication No. 7-180081 A

Patent document 2: Japanese Patent Publication No. 7-233494 A

SUMMARY OF INVENTION

Problems that the Invention is to Solve

An object of the present invention is to provide a nickel-iron alloy plating solution which can suppress, in a nickel-iron alloy plating solution containing divalent iron ions, the oxidation of divalent iron ions to trivalent iron ions and can prevent the occurrence of the precipitation of iron (III) hydroxide to allow stable continuous operations. Another object of the present invention is to provide a nickel-iron alloy plating solution which allows the production of a soft magnetic film which is stable in composition. 30

Means for Solving the Problems

The present inventor has carried out extensive studies and found that the above problems can be solved by using a specific reducing agent and adjusting the pH to a specific range to accomplish the present invention.

Thus, the present invention provides the following:

(1) a nickel-iron alloy plating solution characterized in that it comprises divalent iron ions, divalent nickel ions and a hydroxylamine salt and has a pH of 3.0 or lower, wherein a concentration of the hydroxylamine salt is 1/100 to 1/2 as a molar ratio to that of the divalent iron ions;

(2) the nickel-iron alloy plating solution according to the above (1), wherein the pH is 2.5 or higher and 3.0 or lower;

(3) the nickel-iron alloy plating solution according to the above (1) or (2), wherein a concentration of the divalent iron ions is 4 to 18 mmol/L, a concentration of the divalent nickel ions is 150 to 500 mmol/L and a molar ratio of the divalent nickel ions to the divalent iron ions (divalent nickel ions/divalent iron ions) is 10 or more and 40 or less;

(4) the nickel-iron alloy film obtained by carrying out electroplating with the nickel-iron alloy plating solution according to any one of the above (1) to (3), characterized in that the nickel-iron alloy film has an iron content of 18% by mass or more and 22% by mass or less and a coercivity of 0.5 Oe or less. 55 60

Advantageous Effects of Invention

According to the nickel-iron alloy plating solution of the present invention, the oxidation of divalent iron ions in the

nickel-iron alloy plating solution containing divalent iron ions can be suppressed and occurrence of the precipitation of iron (III) hydroxide can be prevented, so that continuous plating can be carried out stably for long periods.

According to the present plating solution, the iron content in plating films can be controlled, so that soft magnetic nickel-iron alloy films which are stable in composition can be obtained.

MODE FOR CARRYING OUT THE INVENTION

When a nickel-iron alloy plating solution containing divalent iron ions is left over, iron ions are oxidized to be trivalent iron ions and iron (III) hydroxide is precipitated. During plating, divalent iron ions are oxidized to trivalent iron ions at the anode side, resulting in the occurrence of the precipitation of iron (III) hydroxide. It has been found that the addition of a reducing agent is effective for suppressing the oxidation of divalent iron ions, which is particularly hydroxylamine salts (inorganic acid salts of hydroxylamine such as hydroxylamine hydrochloride, hydroxylamine sulfate, hydroxylamine nitrate, hydroxylamine phosphate and hydroxylamine carbonate; and organic acid salts of hydroxylamine such as hydroxylamine oxalate and hydroxylamine acetate), with inorganic acid salts of hydroxylamine being more effective among others and addition of hydroxylamine sulfate being particularly effective.

It is also important that the plating solution has a pH of 3.0 or lower. Due to this pH of 3.0 or lower, the occurrence of the precipitation of iron (III) hydroxide can be prevented. By reducing the pH, spontaneous decomposition of the hydroxylamine salt is suppressed, so that the suppression effect of the oxidation of divalent iron ions is enhanced. By reducing the pH, the solubility of the iron ions are also increased, so that the precipitation of hydroxides occur less, even when divalent iron ions are oxidized to trivalent iron ions. However, the decrease in pH tends to cause an increased amount of hydrogen gas to be produced at the cathode and a decreased current efficiency and iron content in the deposited films. In order to obtain films having an iron content of 18% by mass or more, the pH needs to be 2.5 or higher. When the pH exceeds 3.0, divalent iron ions are immediately oxidized and the precipitation of iron (III) hydroxide occurs. Thus, the pH is preferably 2.5 or higher and 3.0 or lower in order to obtain films having an iron content of 18% by mass or more.

The nickel-iron alloy plating solution of the present invention can be obtained by dissolving at least a divalent iron ion source compound, a divalent nickel ion source compound and a hydroxylamine salt as a reducing agent in water and adjusting the pH to 3.0 or lower. Alternatively, it is also possible to preliminarily prepare an aqueous solution containing divalent iron ions by dissolving the divalent iron ion source compound and the hydroxylamine salt in water and then dissolve the divalent nickel ion source compound into the solution.

By preliminarily preparing the aqueous solution containing divalent iron ions which is a concentrated solution, transportation costs are decreased and the initial make-up of the bath is facilitated compared to the case where a powder is dissolved, because it can be used after dilution with water. The above solution can be also used as an iron ion supplementary solution.

The divalent iron ion source compound may include iron (II) sulfate, iron (II) chloride and the like.

The divalent nickel ion source compound may include nickel (II) chloride, nickel (II) sulfate, nickel (II) nitrate, nickel (II) acetate, nickel (II) sulfamate and the like.

Nickel (II) chloride contributes as, in addition to as a nickel ion source, a chloride ion source. It can also facilitate the dissolution of nickel as an ion from a nickel anode during electroplating due to the corrosive properties of chloride ions. On the other hand, when it exists in excess, film hardness and internal stress are increased. Thus, an appropriate control thereof is necessary.

A pH adjusting agent may include sulfuric acid, hydrochloric acid, sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide and the like.

The amount of the hydroxylamine salt to be added is preferably 1/100 or more as a molar ratio relative to the divalent iron ions, in view of the suppression effect of the oxidation of the divalent iron ions. Basically, the higher the concentration of the hydroxylamine salt is, the higher the suppression effect of the oxidation of the divalent iron ions. However, when the concentration of the reducing agent is high in nickel-iron alloy plating solutions, the iron content in the resulting plating films is decreased. With the decomposition of the hydroxylamine salt, the iron content in the plating films is gradually increased, so that variations in composition of iron in the plating films are increased when the amount of the reducing agent is too high. Thus, the concentration of the hydroxylamine salt in the nickel-iron alloy plating solution is preferably 1/100 to 1/2 as a molar ratio relative to that of divalent iron ions, and more preferably 1/25 to 1/2.

The concentration of divalent iron ions in the plating solution of the present invention is preferably 4 to 18 mmol/L. When the concentration of divalent iron ions is lower than 4 mmol/L, the iron content in the plating films obtained during plating cannot be 18% by mass or more, thus soft magnetic films cannot be obtained. When it is higher than 18 mmol/L, the required amount of the hydroxylamine salt, added along with iron ions and having reducing action on the iron ions, is increased; thus, when the concentration of the hydroxylamine salt is too high, the iron content in the plating films obtained during plating tends to be decreased. With decomposition of the hydroxylamine salt, the iron content in the plating films is gradually increased; thus in order to maintain the iron content at a constant level, the concentration of iron ions in the plating solution and stirring speed need to be altered. Accordingly, the conditions for plating need to be changed all the time, rendering plating procedures complicated.

It is preferable that the concentration of divalent nickel ions in the plating solution of the present invention is in the range of 150 mmol/L to 500 mmol/L and that a molar ratio of divalent nickel ions to divalent iron ions (divalent nickel ions/divalent iron ions) is 10 or more and 40 or less.

When the concentration of divalent nickel ions is lower than 150 mmol/L, hydrogen generation during plating is vigorous, merely resulting in significantly tarnished plating films. When the concentration is higher than 500 mmol/L, the solubility of nickel ions reaches to a limit in the context of other salts. When the molar ratio to divalent iron ions is outside of the above range, plating films having a composition of an iron content of 18 to 22% by mass cannot be obtained, even when plating conditions such as cathode current density are varied.

The nickel-iron alloy plating solution of the present invention may comprise, in addition to the divalent iron ion source compound, a divalent nickel ion source compound and the

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hydroxylamine salt, well-known additives such as pH buffers, electroconductive salts, stress release agents and surfactants.

pH buffers may include boric acid, citric acid, succinic acid, ascorbic acid and the like.

Electroconductive salts may include ammonium chloride, ammonium sulfate and the like.

Stress release agents may include saccharin, 1,4-buthyn-diol and the like.

Surfactants may include lauryl sulfuric acid and its salts, alkylbenzene sulfonates, fatty acid triethanolamine salts and the like.

Nickel-iron alloy electroplating is preferably carried out at a bath temperature of 20 to 60° C. and a cathode current density of 1 to 2 A/dm² while the solution is thoroughly stirred e.g. with a paddle.

A material to be plated is preferably wafers whose outermost surface is coated with an electroconductive metal (nickel-iron alloy, copper etc.) to be used as an electrode for electroplating.

The plating film formed with the nickel-iron alloy plating solution of the present invention is preferably a soft magnetic film having an iron content of 18% by mass or more and 22% by mass or less and a coercivity of 0.5 Oe or less. When the plating film has an iron content of 18% by mass or more, the coercivity of the film corresponds to a soft magnetic property of 0.5 Oe (Oersted) or less. On the other hand, when the film has an iron content of less than 18% by mass, the coercivity of the film is sharply increased and the film does not exhibit a soft magnetic property any more. When the iron content exceeds 22% by mass, the concentration of iron ions in the plating solution is high; thus the suppression effect of the occurrence of the precipitation of iron (III) hydroxide is not sufficient, even with the reducing agent being added, and precipitation occurs after plating.

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EXAMPLES

The present invention is now illustrated by means of examples.

Examples 1 to 3 and Comparative Examples 1 to 3

A solution having the following compositions: 168 mmol/L nickel (II) chloride; 76 mmol/L nickel (II) sulfate; 11 mmol/L iron (II) sulfate; 404 mmol/L boric acid; 187 mmol/L ammonium chloride; 5.5 mmol/L saccharin; pH 2.7 (sulfuric acid) supplemented with a substance having reduction activity on divalent iron ions or a complexing agent in an amount shown in Table 1 was used for nickel-iron electroplating on a sputtered nickel-iron film formed on a wafer at a bath temperature of 25° C. and a cathode current density of 1.5 A/dm² for 20 minutes while stirring the solution to obtain a nickel-iron alloy plating film having a film thickness of 5 μm. The iron content in the obtained nickel-iron alloy plating film was measured with an EDS (energy dispersive x-ray spectroscopy).

The magnetizing properties of the nickel-iron alloy plating film were measured with a vibrating sample magnetometer (VSM) from Riken Denshi Co., Ltd., and the obtained hysteresis curve was used to obtain coercivity.

The presence or absence of the precipitation of iron (III) hydroxide in the plating solution after plating was examined.

The results are summarized in Table 1.

TABLE 1

	Concentration of iron (II) sulfate (mmol/L)	Reducing agent (complexing agent)	Concentration of reducing agent (complexing agent) (mmol/L)	Molar ratio of reducing agent (complexing agent)/iron sulfate	pH	Fe content in Ni—Fe alloy (%) by mass	Coercivity of Ni—Fe film (Oe)	Occurrence of precipitation after plating
Example 1	11	Hydroxylamine sulfate	0.55	1/20	2.7	19.8	0.45	No
Example 2	11	Hydroxylamine hydrochloride	4.4	1/2.5	2.7	18.2	0.48	No
Example 3	11	Hydroxylamine nitrate	6.5	1/1.7	2.7	17.8	0.96	No
Comparative Example 1	11	L(+)-ascorbic acid	0.55	1/20	2.7	19.4	0.44	Yes
Comparative Example 2	11	Malonic acid	4.4	1/2.5	2.7	17.8	1.19	No
Comparative Example 3	11	Adipic acid	6.5	1/1.7	2.7	17.7	1.31	No

The plating film having an iron content of 18% by mass or more and 22% by mass or less and a coercivity of 0.5 Oe or less, which is formed with the nickel-iron alloy plating solution of the present invention, can be suitably used as materials for magnetic shieldings and the like.

The film thickness of the plating film is preferably 1 to 10 μm.

The ratio by mole of the reducing agent to iron sulfate of 1/2 separates the iron content in the obtained plating films above or below 18% by mass. When the iron content is 18% by mass or more, the coercivity of the film is a soft magnetic property of 0.5 Oe (Oersted) or less, while the film having an iron content of less than 18% by mass has sharply increased coercivity and does not show a soft magnetic property.

When L(+)-ascorbic acid was used as the reducing agent, the precipitation of iron (III) hydroxide occurred after plating (Comparative Example 1).

When complexing agents were used instead of reducing agents, the plating films had the iron content of less than 18% by mass as well as the coercivity of 0.5 Oe or more and did not show a soft magnetic property (Comparative Examples 2 and 3).

Example 4

A solution having the following compositions: 84 mmol/L nickel (II) chloride; 152 mmol/L nickel (II) sulfate; 8 mmol/L iron (II) sulfate; 323 mmol/L boric acid; 280 mmol/L ammonium chloride; 11 mmol/L saccharin; pH 2.7 (sulfuric acid) supplemented with 0.8 mmol/L hydroxylamine sulfate was used for nickel-iron electroplating on a sputtered copper film formed on a wafer at a bath temperature of 55° C. and a cathode current density of 1.5 A/dm² for 20 minutes while stirring the solution to obtain a nickel-iron alloy plating film having a film thickness of 5 μm. The same measurements and evaluations were carried out as Example 1. The results are summarized in Table 2.

The obtained plating film had an iron content in the range of 18% by mass or more and 22% by mass or less and a coercivity of 0.5 Oe or less. No precipitation occurred in the plating solution after plating.

Example 5

A solution having the following compositions: 126 mmol/L nickel (II) chloride; 114 mmol/L nickel (II) sulfate; 16 mmol/L iron (II) sulfate; 243 mmol/L boric acid; 374 mmol/L ammonium chloride; 8.2 mmol/L saccharin; pH 2.7 (hydrochloric acid) supplemented with 1.6 mmol/L hydroxylamine hydrochloride was used for nickel-iron electroplating on a sputtered nickel-iron film formed on a wafer at a bath temperature of 55° C. and a cathode current density of 1.5 A/dm² for 20 minutes while stirring the solution to obtain a

Example 6

A solution having the following compositions: 168 mmol/L nickel (II) chloride; 76 mmol/L nickel (II) sulfate; 11 mmol/L iron (II) sulfate; 404 mmol/L boric acid; 187 mmol/L ammonium chloride; 5.5 mmol/L saccharin; pH 2.3 (hydrochloric acid) supplemented with 1.1 mmol/L hydroxylamine nitrate was used for nickel-iron electroplating on a sputtered copper film formed on a wafer at a bath temperature of 25° C. and a cathode current density of 1.5 A/dm² for 20 minutes while stirring the solution to obtain a nickel-iron alloy plating film having a film thickness of 5 μm. The same measurements and evaluations were carried out as Example 1. The results are summarized in Table 2.

The obtained plating film had an iron content of less than 18% by mass and a coercivity of far more than 0.5 Oe. No precipitation occurred in the plating solution after plating.

Comparative Example 4

A solution having the following compositions: 168 mmol/L nickel (II) chloride; 76 mmol/L nickel (II) sulfate; 11 mmol/L iron (II) sulfate; 404 mmol/L boric acid; 187 mmol/L ammonium chloride; 5.5 mmol/L saccharin; pH 3.2 (hydrochloric acid) supplemented with 1.1 mmol/L hydroxylamine hydrochloride was used for nickel-iron electroplating on a sputtered copper film formed on a wafer at a bath temperature of 25° C. and a cathode current density of 1.5 A/dm² for 20 minutes while stirring the solution to obtain a nickel-iron alloy plating film having a film thickness of 5 p.m. The same measurements and evaluations were carried out as Example 1. The results are summarized in Table 2.

The obtained plating film had an iron content of more than 22% by mass. Although it had a coercivity of 0.5 Oe or less, a significant amount of precipitation was generated in the plating solution after plating.

TABLE 2

	Concentration of iron (II) sulfate (mmol/L)	Reducing agent	Concentration of reducing agent (mmol/L)	Molar ratio of reducing agent/iron sulfate	pH	Fe content in Ni—Fe alloy (%) by mass)	Coercivity of Ni—Fe film (Oe)	Occurrence of precipitation after plating
Example 4	8	Hydroxylamine sulfate	0.8	1/10	2.7	18.8	0.46	No
Example 5	16	Hydroxylamine hydrochloride	1.6	1/10	2.7	21.1	0.48	No
Example 6	11	Hydroxylamine nitrate	1.1	1/10	2.3	17.2	1.82	No
Comparative Example 4	11	Hydroxylamine hydrochloride	1.1	1/10	3.2	22.3	0.47	Yes

nickel-iron alloy plating film having a film thickness of 5 μm. The same measurements and evaluations were carried out as Example 1. The results are summarized in Table 2.

The obtained plating film had an iron content in the range of 18% by mass or more and 22% by mass or less and a coercivity of 0.5 Oe or less. No precipitation occurred in the plating solution after plating.

The invention claimed is:

1. A nickel-iron alloy plating solution comprising divalent iron ions, divalent nickel ions and a hydroxylamine salt and having a pH of no more than 3.0, wherein the concentration of the hydroxylamine salt is 1/100 to 1/2 as a molar ratio to that of the divalent iron ions, the concentration of the divalent iron ions is 4 to 18 mmol/L, the concentration of the divalent

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nickel ions is 150 to 500 mmol/L and the molar ratio of the divalent nickel ions to divalent iron ions is from 10/1 to 40/1.

2. The nickel-iron alloy plating solution according to claim 1, wherein the pH is from 2.5 to 3.0.

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